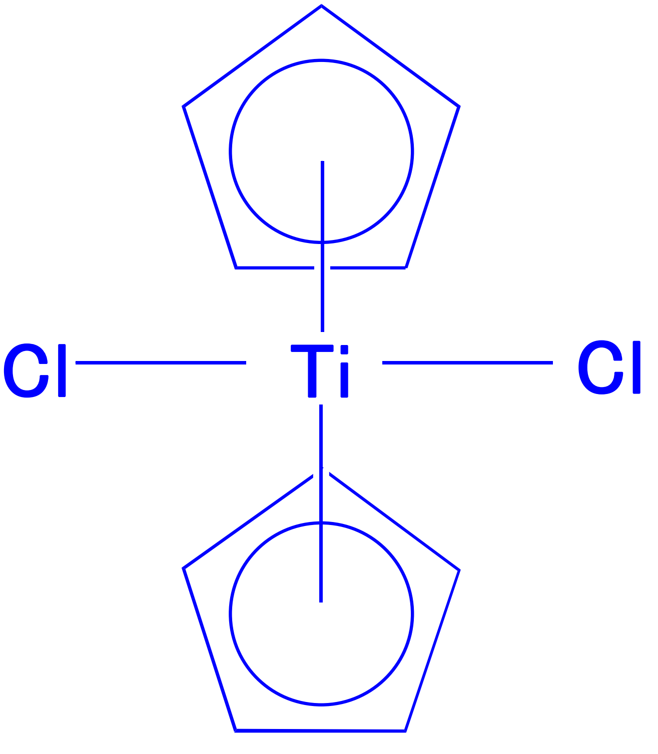
Titanocene Dichloride

Technical Data



NICHIA CORPORATION

CONTENTS

1. General Features

(1) Titanocene Dichloride highly acts on the unsaturated compounds and shows excellent effects as an active homogeneous hydrogenation catalyst under moderate conditions.
(2) Titanocene Dichloride improves stereo regularity due to the effect of cyclopentadienyl group.
(3) Titanocene Dichloride can be widely used for various derivatives which become the basic materials for high performance chemical products.
(4) Consistently high/uniform quality has been realized by the strict manufacturing process/quality control.

We have strong customer-service engineering team in our V-plant listed on the last page. Please feel free to contact us at the nearest Nichia sales office if you are interested in this product or other Titanocene derivatives.

2. Product Guide

2－1. Physical and Chemical Properties

Chemical Name : Bis-Cyclopentadienyl Titanium Dichloride
Titanocene Dichloride

Molecular Formula : $(C_5H_5)_2TiCl_2$

Molecular Weight : 248. 99

Appearance : Red ～ Reddish-brown crystalline powder

Melting Point : 287～293 ℃

Sublimation Point : 160 ℃ (13 Pa)

Solubility : Soluble in Halogenated Hydrocarbon,
Aromatic Hydrocarbon and Protic Solvents.
Slightly Soluble in Aliphatic Hydrocarbon.

Decomposability : Titanocene Dichloride gradually decomposes by the moisture and the oxygen in air if left in the open air.
Titanocene Dichloride is relatively stable against heat.

2－2. Assay and Impurities

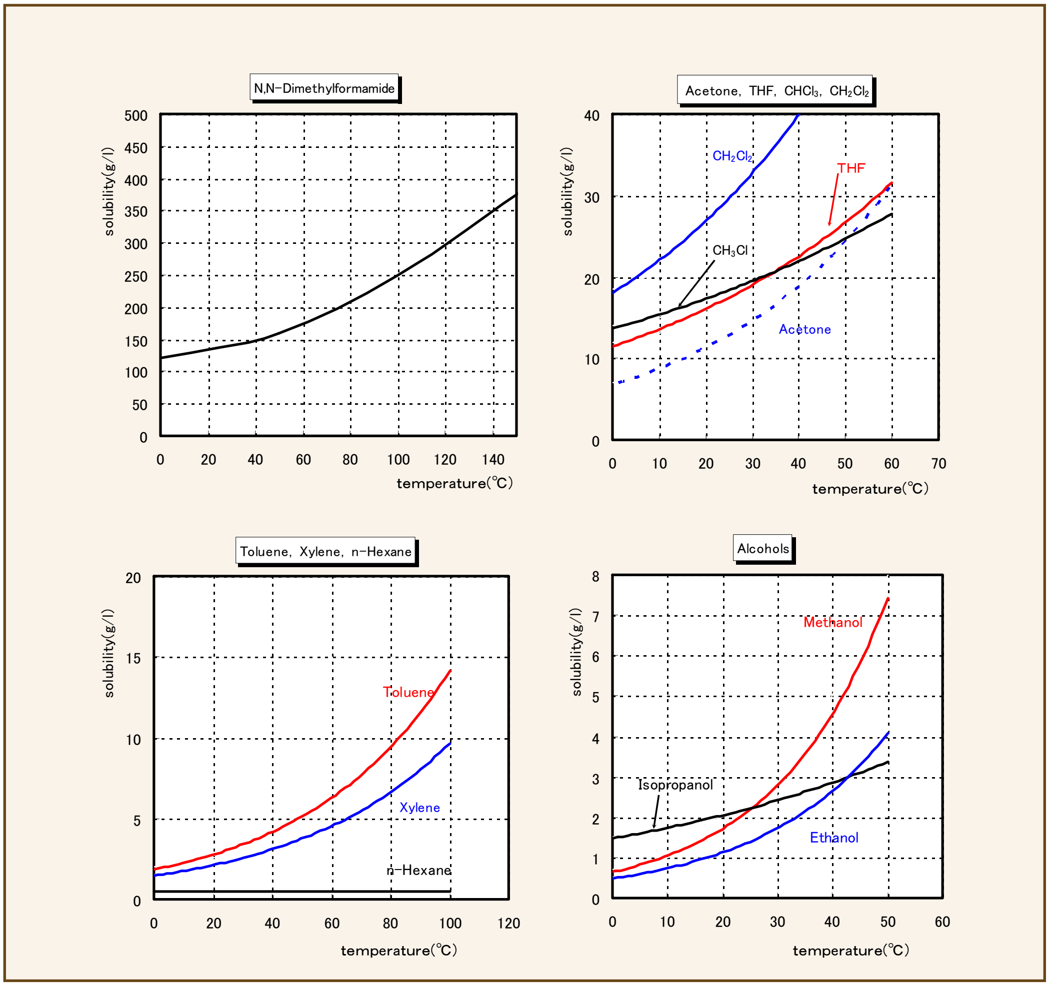
		Specifications	Typical Data	Theoretical Value
Titanium (Ti)	:	≧ 19. 15%	19. 18%	19. 24%
Chlorine (Cl)	:	≧ 28. 35%	28. 40%	28. 48%
Iron (Fe)	:	≦ 0. 01%	0. 0005%	

Analytical Data of Titanocene Dichloride

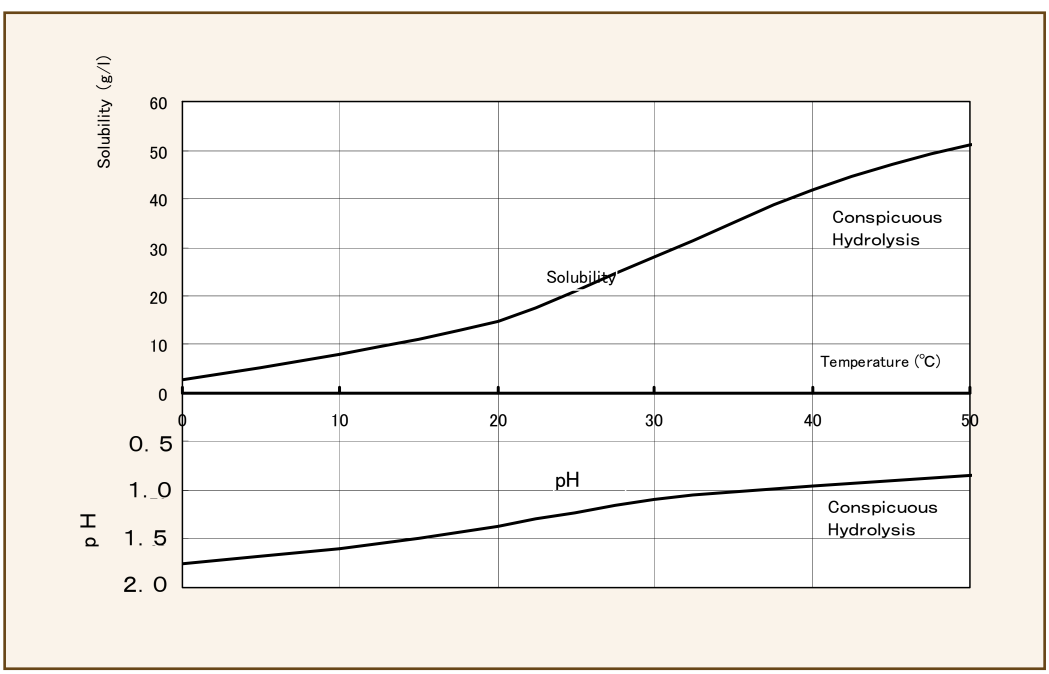
Suppliers	Ti(%)	Cl(%)	Cl/Ti (Molar Ratio)	Notes
Nichia	19.18	28.40	2.00	Crystalline Powder Narrow PSD, Fe: 5 ppm LC Purity: ≧99%
Reagent A	19.26	28.32	1.99	Crystalline Powder Broad PSD
Reagent B	18.50	27.82	2.03	Powder
Reagent C	18.88	28.11	2.01	Crystalline Powder Broad PSD
Reagent D	19.19	28.16	1.98	Crystalline Powder Broad PSD, Fe: 154 ppm
Reagent E	18.83	28.34	2.03	Crystalline Powder Broad PSD, Fe: 25 ppm
Reagent F	18.83	27.82	2.00	Crystalline Powder Broad PSD, Fe: 32 ppm
Theoretical Value	19.24	28.48	2.00	

Ti and Cl contents were determined in Nichia.

3. Solubility in Various Solvents

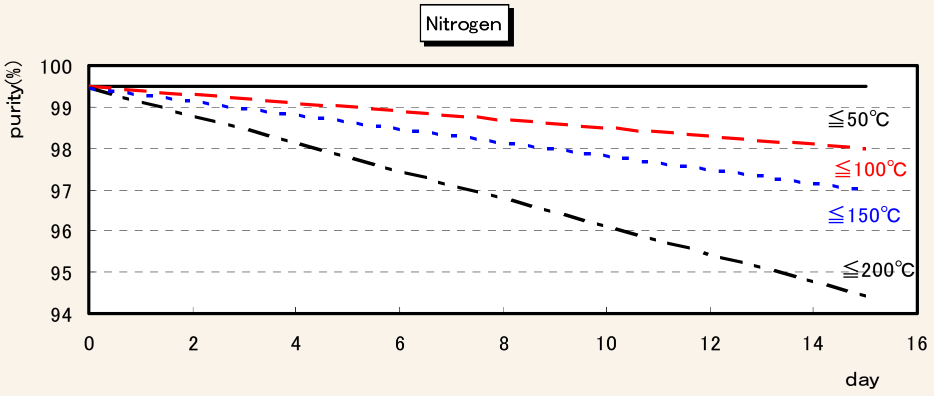


4. Solubility in Water and pH

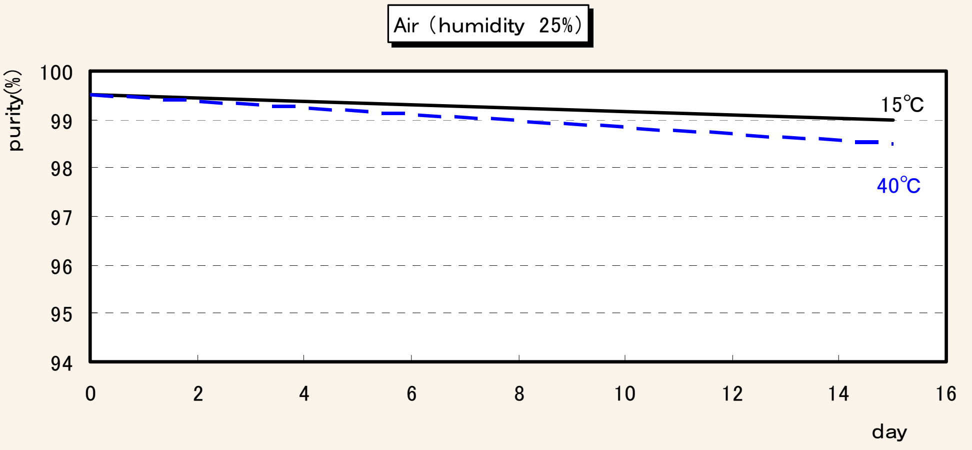


5. Stability

(1) Titanocene Dichloride is stable in nitrogen atomosphere under 50℃ and its purity will not deteriorate.



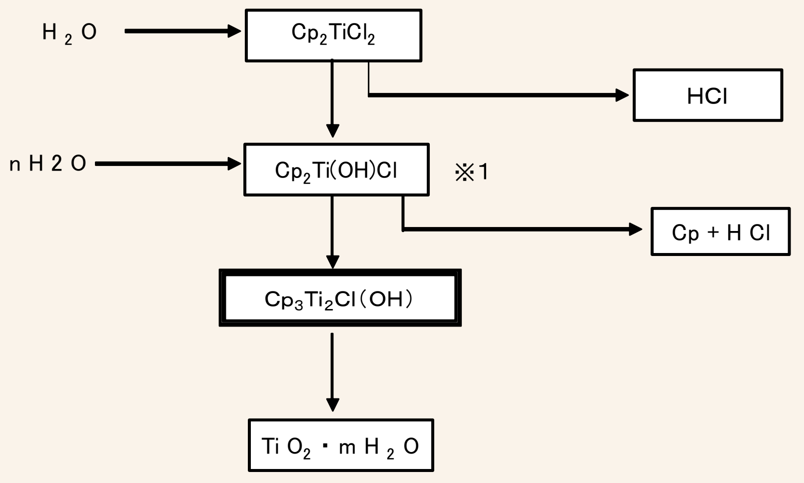
(2) In open air its quality will deteriorate due to hydrolysis and influence of oxygen.



(3) Its quality will deteriorate under the influence of ultraviolet rays.

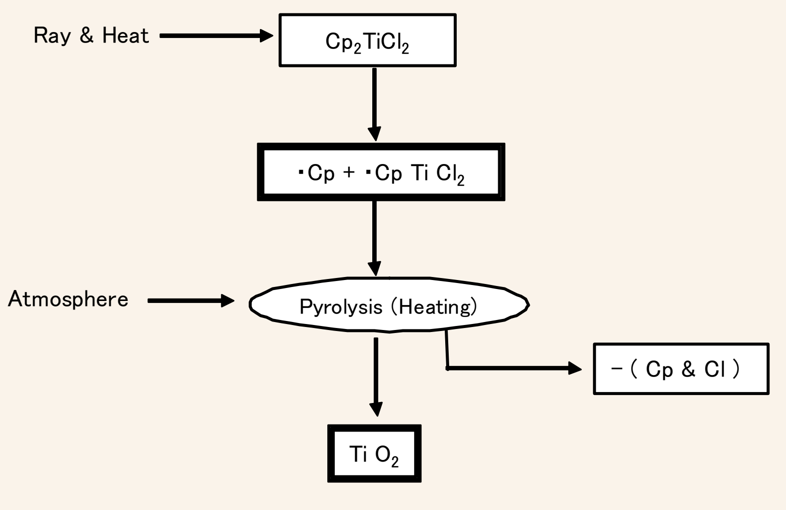
6. Decomposition Mechanism

1. Hydrolysis



※1: G. Wilkinson, F.A. Cotton, Progress in Inorganic Chemistry,1, 1-124 (1959)

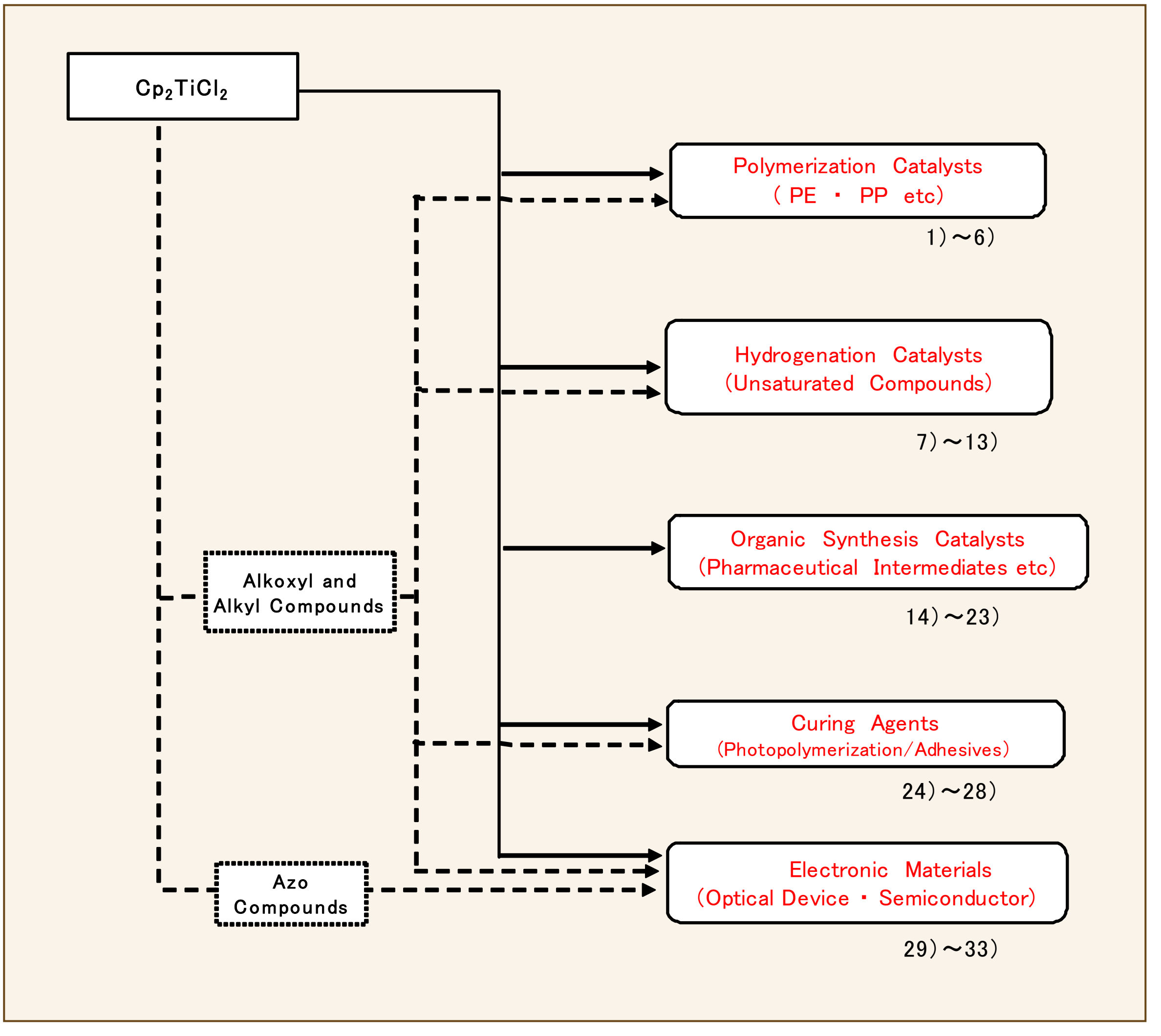
2. Photolysis and Pyrolysis



▭ : Identified Substances

540℃…All Anatase Type
750℃…Anatase Type and Rutile Type Mixtures
950℃…All Rutile Type

7. Applications (Examples)



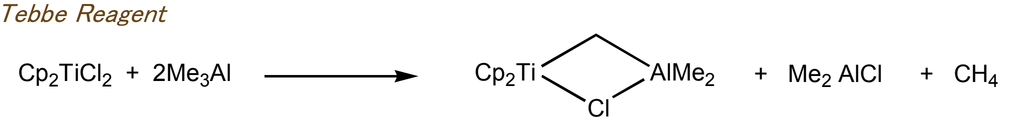
References of Applications

1)J. Polym. Sci., 3, 1729 (1965) 2)Polym. Sci. Technol., 37, 239 (1988)
3)JP 01282214 A 4)DD 237671 A1 5)DD 282013 A5 6)JPH 8−12716 A
7)Am. Chem. Soc. Div. Pet. Chem. 27, 816 (1982) 8)J. Am. Chem. Soc. 85, 4014 (1965)
9)JPH 7−90017 A 10)JPH 11−071426 A 11) J. Organomet. Chem. 382, 69 (1990)
12)J. Organomet. Chem. 384, C17−20 (1990) 13)USP−529807 (1990)
14)Angew. Chem. Int Ed Eng 18, 477 (1979) 15)J. Organomet. Chem. 302, 281(1986)
16)Huaxua Xuebao 46, 703 (1988) 17)J. Am. Chem. Soc. 110, 8561 (1988)
18)Tetrahedron. Lett 31, 3105 (1990) 19)Can. J. Chem. 68, 471 (1990)
20)J. Am. Chem. Soc. 113, 5093 (1991)
21)J. Chem. Soc. Chem. Commun., 13, 941 (1992)
22)J. Am. Chem. Soc., 114, 2276 (1992)
23)EP 407804 A1 24)Proceedings of Conference on Radiation Curing Asia 461 (1988)
25)JPS 63−41484 A (or CHP 3101/86−2) 26)JPH 4−47680 B
27)JPH 6−65549 A 28)EP 401166 A2 29)J. Organometal Chem. 111, 297 (1976)
30)Appl. Phys. Lett., 43, 992 (1983)
31)Proc Int Conf Chem Vapor Deposition., 11, 703 (1990)
32)JPH 6−65549 A 33)JPH 4−235994A

8. Application of Cp_2TiCl_2 in Organic Synthesis

Synthesis of Methylenation Reagent

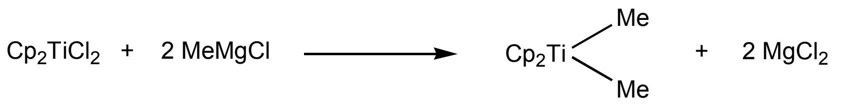
○ *Tebbe Reagent*



Tebbe Reagent

J. Am. Chem. Soc., 100, 3611 (1978)

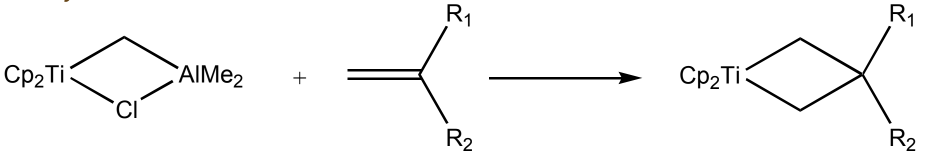
○ *Petasis Reagent*



Petasis Reagent

J. Am. Chem. Soc., 112, 6392 (1990)

○ *Titanacyclobutane*

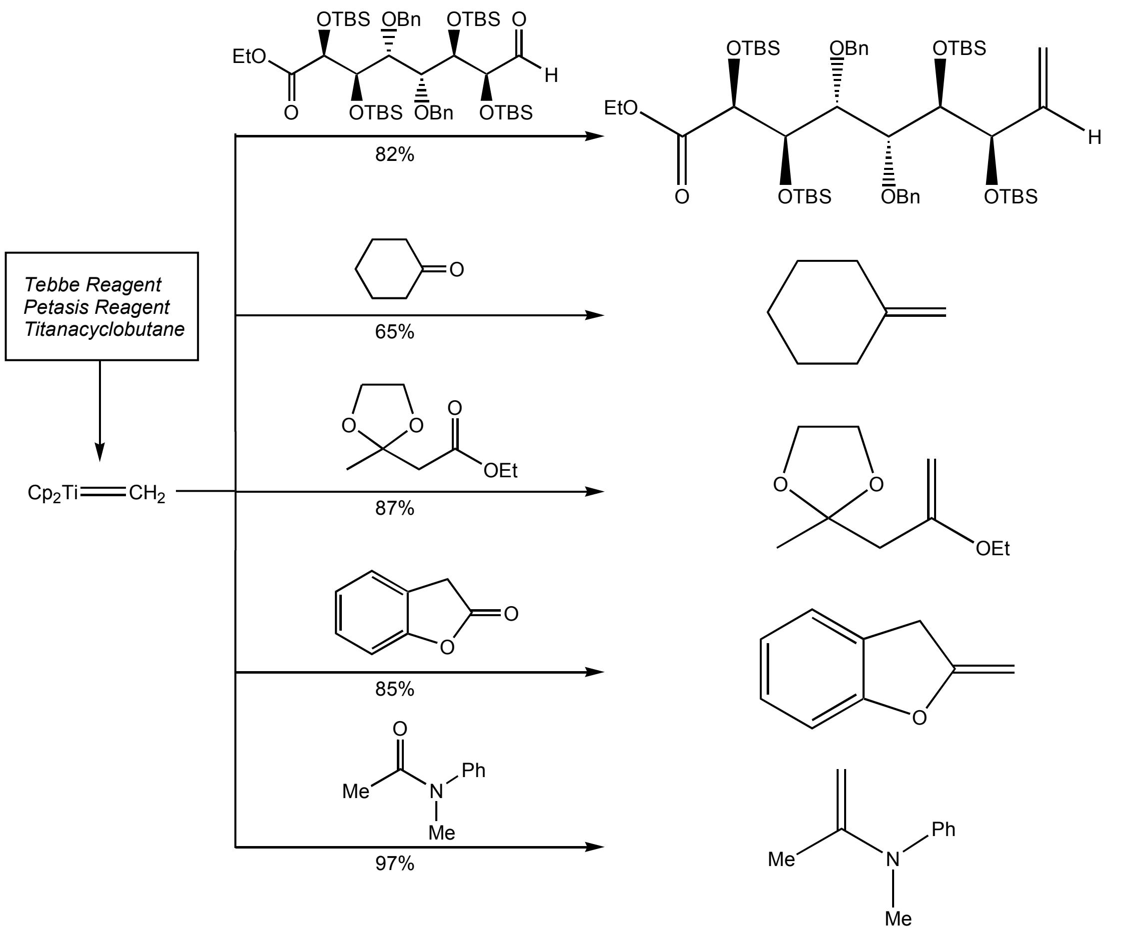


Tebbe reagent

Titanacyclobutane

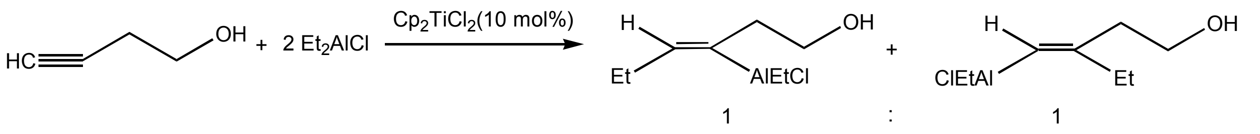
J. Am. Chem. Soc., 102, 6876 (1980)

Methylenation of Aldehydes, Ketones, Esters, Lactones, and Amides



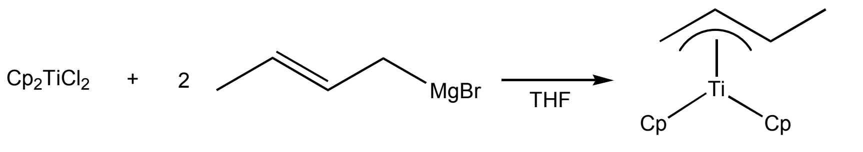
J. Am. Chem. Soc., 114, 2524 (1992)
J. Am. Chem. Soc., 100, 3611 (1978)
J. Am. Chem. Soc., 102, 3270 (1980)
J. Org. Chem., 50, 1212 (1985)

Cp_2TiCl_2–Catalyzed Carbometalation of Alkynols



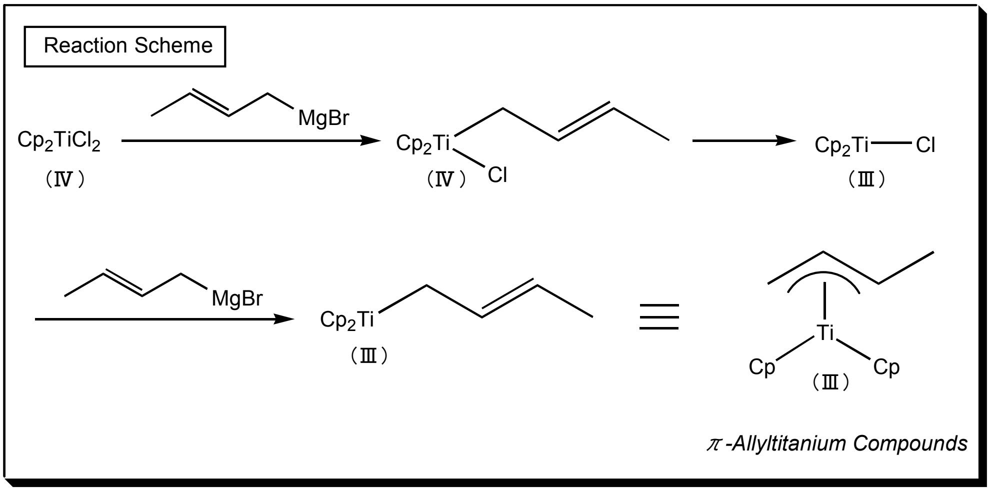
J. Org. Chem., 44, 3457 (1979)

π–Allyltitanium Compounds in Organic Synthesis

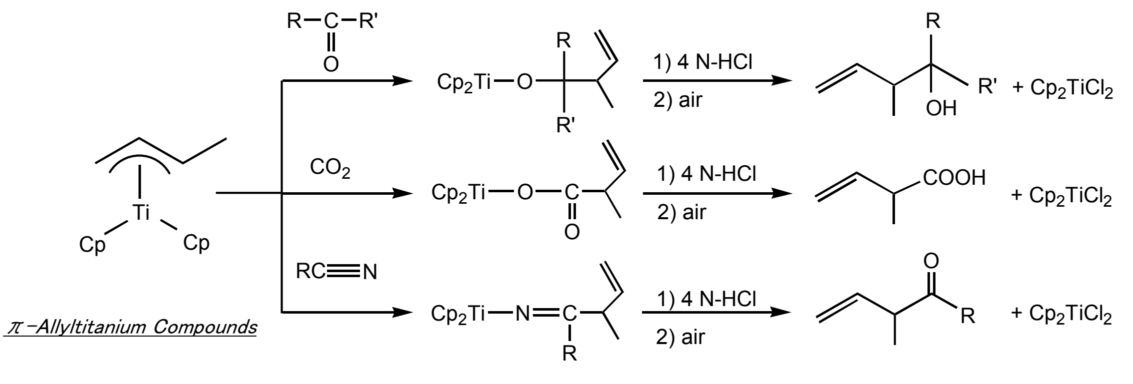


π-Allyltitanium Compounds

J. Organometal. Chem., 8, 115 (1967)



○ *Insertion Reactions*



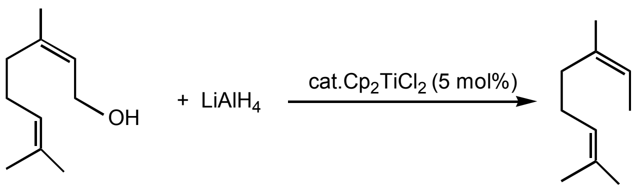
J. Chem. Soc., Chem. Commun., 342 (1981)
Tetrahedron Lett., 22, 243 (1981)
J. Chem. Soc., Chem. Commun., 180 (1981)

Hydroalumination of Olefins Catalyzed by Cp_2TiCl_2

$NaAlH_4$ + $4RCH{=}CH_2$ —(cat.Cp_2TiCl_2 (5 mol%))→ $NaAl(CH_2CH_2R)_4$

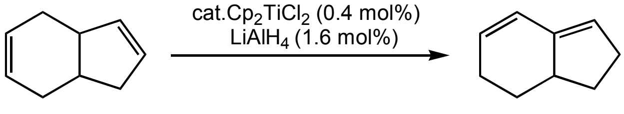
J. Org. Chem., 45, 1035 (1980)

Hydrogenolysis of Allylalcohols Catalyzed by Cp_2TiCl_2



Chem. Lett., 103 (1980)

Isomerization Catalyzed by Cp_2TiCl_2



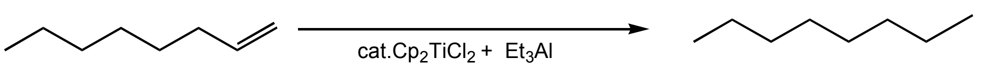
Tetrahedron Lett., 21, 637 (1980)

Olefin Metathesis Catalyzed by Cp_2TiCl_2

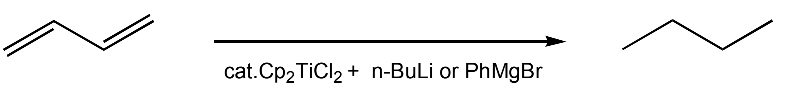
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOEt$ ⇌ (WCl_6 (10 mol%), Cp_2TiMe_2 (12 mol%)) $EtO_2C(CH_2)_7CH{=}CH(CH_2)_7COOEt$ + $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3$

Tetrahedron Lett., 21, 2955 (1980)

Hydrogenation of Olefins and Conjugated Diolefins Catalyzed by Cp_2TiCl_2



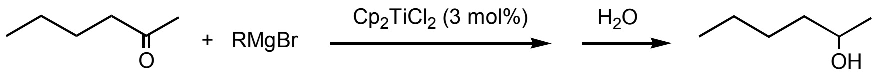
J. Am. Chem. Soc., 85, 4014 (1963)



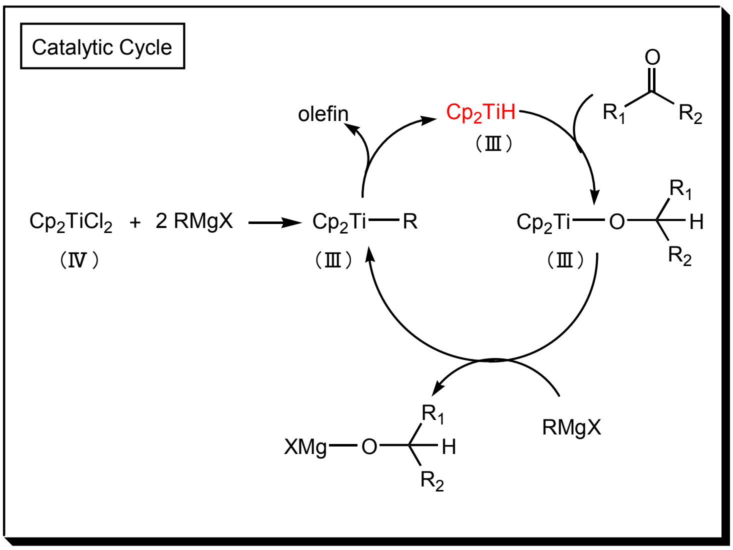
J. Org. Chem., 33, 1689 (1968)

Cp_2TiCl_2–Catalyzed Reduction Using Grignard Reagent

Cp_2TiCl_2–Catalyzed Reduction of Ketones and Aldehydes

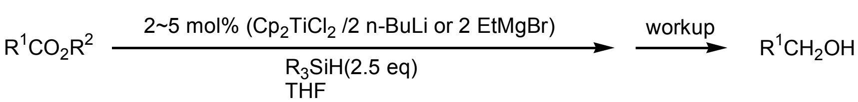


(R=propyl, iso-propyl,2-methylbutyl, hexyl etc.)

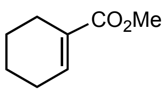
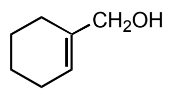
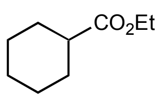
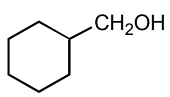
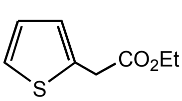
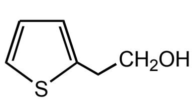


Tetrahedron Lett., 21, 2171 (1980)

Cp_2TiCl_2–Catalyzed Reduction of Esters Using Polymethylhydrosiloxane as the Stoichiometoric Reductant

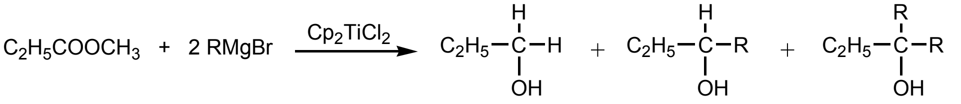


R_3SiH ; poly-(methylhydrosiloxane)

Ester	Product	mol% Cat	n-BuLi or EtMgBr	Time(h)	Yield(%)
$PhCO_2Me$	$PhCH_2OH$	2	EtMgBr	1.5	94
		5	n-BuLi	1	65
		5	EtMgBr	5	88
		5	EtMgBr	17.5	92

J. Org. Chem., 59, 4323 (1994)

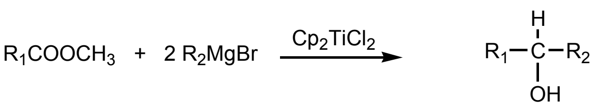
○ *Distribution of The Cp_2TiCl_2-Catalyzed Grignard Reaction Products*



1 2 3

R in RMgBr	mol% of Cp_2TiCl_2	Product Distribution(%) 1	2	3	Total Yield(%)
$CH_3CH_2CH_2$	0	4	0	96	99
	1	9	90	1	97
	4	50	50	0	96
	8	78	22	0	98
$(CH_3)_2CHCH_2$	0	0	60	36	86
	0.13	4	96	0	92
	1	73	27	0	99
	2	96	4	0	94

○ *The Yields of Secondary Alcohols from The Cp_2TiCl_2-Catalyzed Grignard Reactions with Esters*



Secondary Alcohol

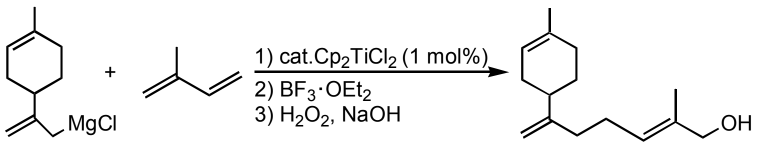
Starting Material: Ester, R_1 in R_1COOCH_3	Starting Material: Grignard Reagent, R_2 in R_2MgBr	Catalyst Content (mol%)	Yield of R_1R_2CHOH (%)
C_6H_{13}	CH_3	1	*
C_6H_{13}	CH_3CH_2	1	*
C_2H_5	$CH_3CH_2CH_2$	1	83
C_6H_{13}		1	81
$(CH_3)_2CH$		1	75
$C_6H_5CH_2$		1	88
C_2H_5	$(CH_3)_2CH$	0.4	74
C_2H_5	$(CH_3)_2CHCH_2$	0.13	85
CH_3	C_6H_{13}	1	91
C_2H_5	C_6H_5	1	*

* No secondary alcohol was obtained.

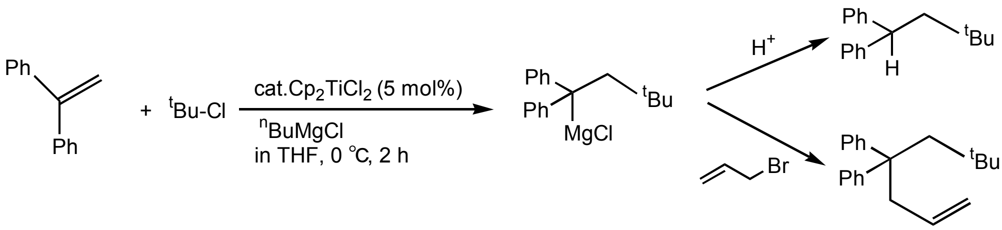
Tetrahedron Lett., 21, 2175 (1980)

Grignard Exchange Reactions of Alkenes, Dienes and Alkynes

○ *Cp_2TiCl_2–Catalyzed Carbomagnesation*

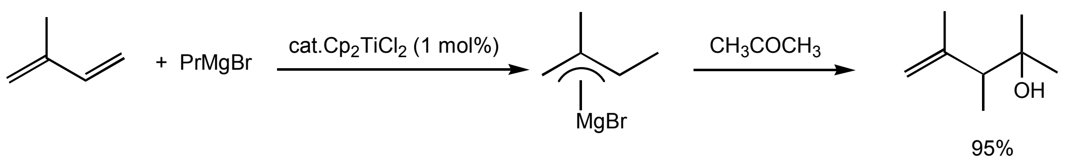


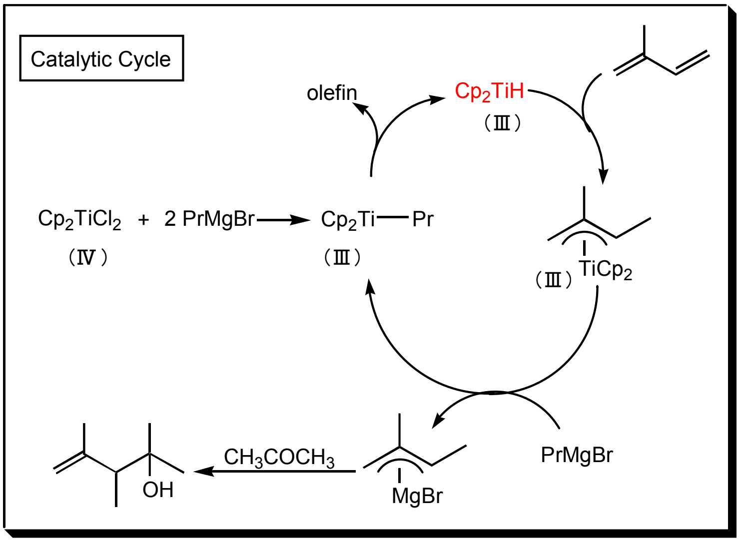
J. Am. Chem. Soc., 97, 6870 (1975)



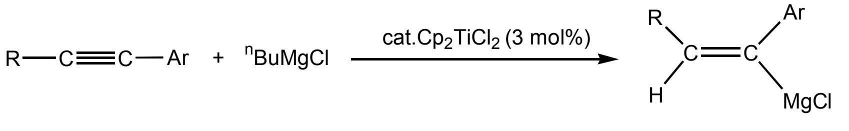
J. Org. Chem., 69, 573 (2004)

○ *Cp_2TiCl_2–Catalyzed Hydromagnesation*





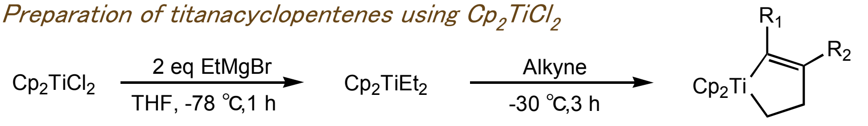
Tetrahedron Lett., 21, 365 (1980)

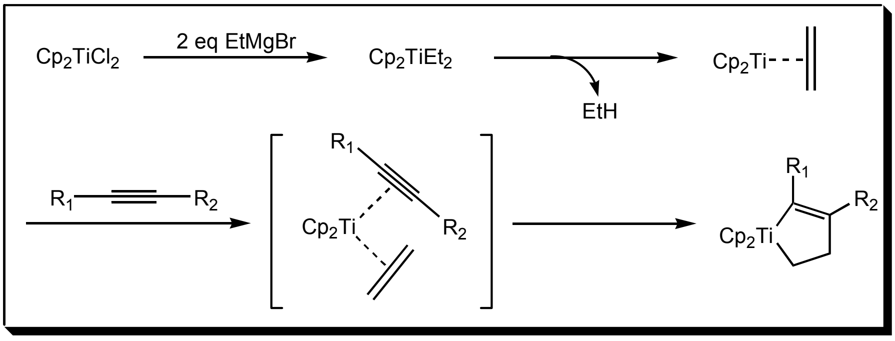


Tetrahedron Lett., 22, 85 (1981)

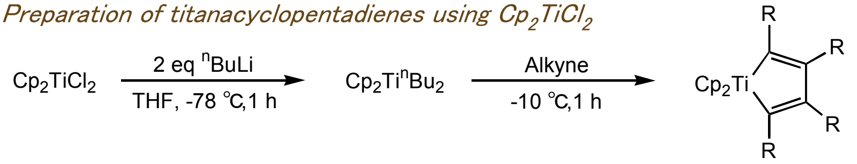
Preparation of titanacyclopentenes and –pentadienes using Cp_2TiCl_2

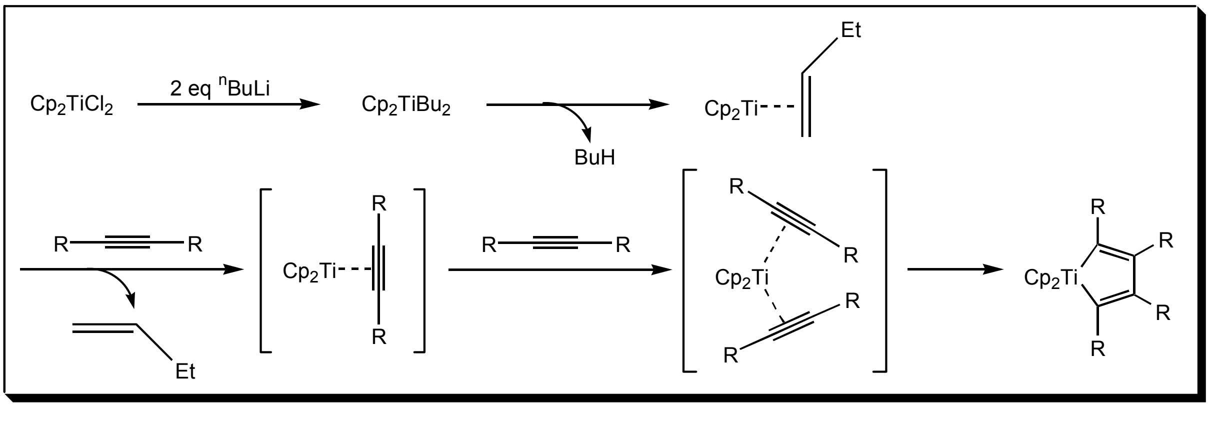
○ *Preparation of titanacyclopentenes using Cp_2TiCl_2*





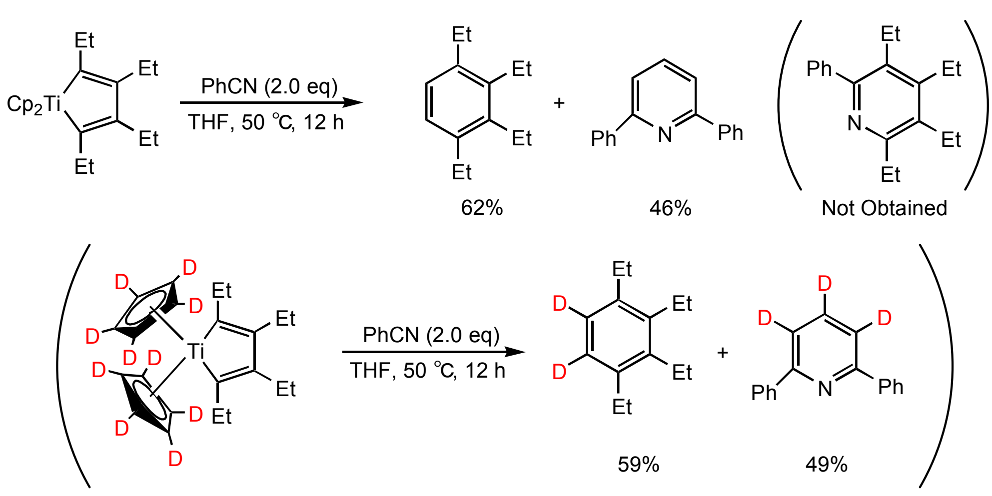
○ *Preparation of titanacyclopentadienes using Cp_2TiCl_2*





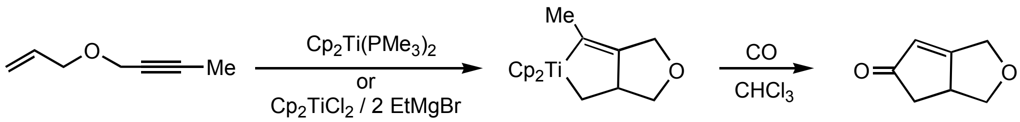
J. Organometal. Chem., 633, 18 (2001)

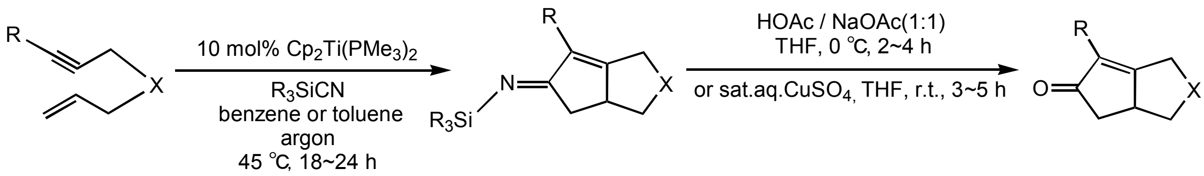
Double C–C bond Cleavage of Cyclopentadienyl Ligand

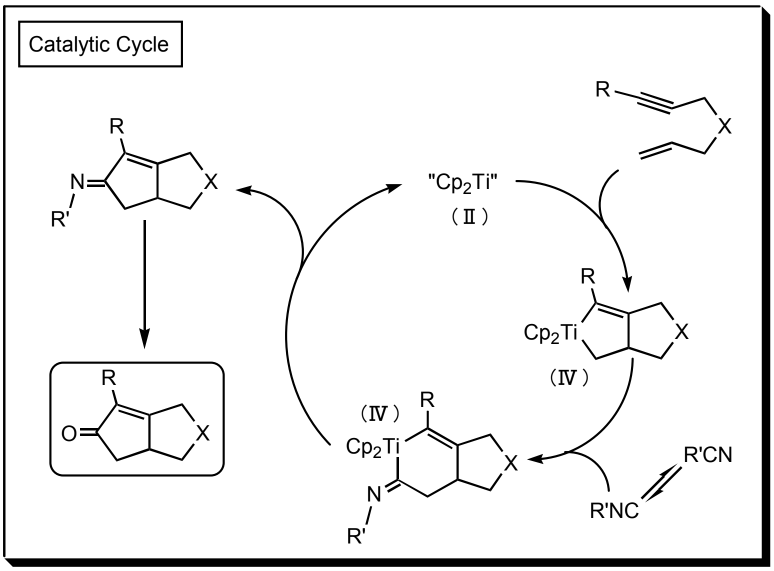


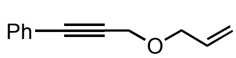
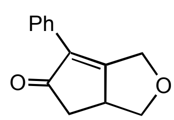
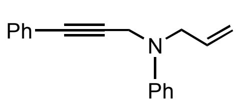
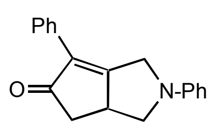
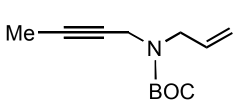
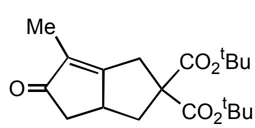
J. Am. Chem. Soc., 125, 9568 (2003)

Enyne Cyclization by Cp_2TiCl_2



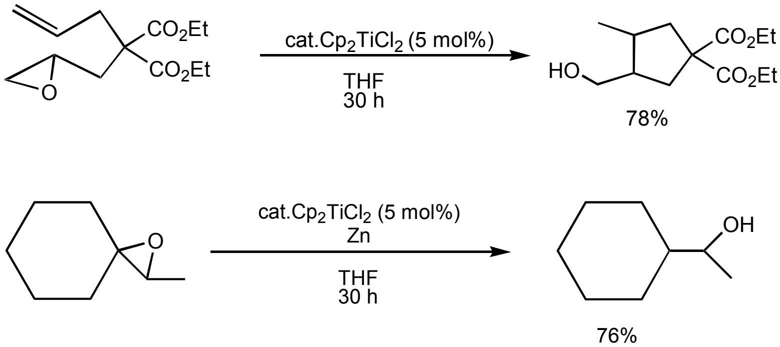




Starting Material	Cyanide	Product	Yield(%)
	Me_3SiCN		80
	Me_3SiCN		44
	Et_3SiCN		43

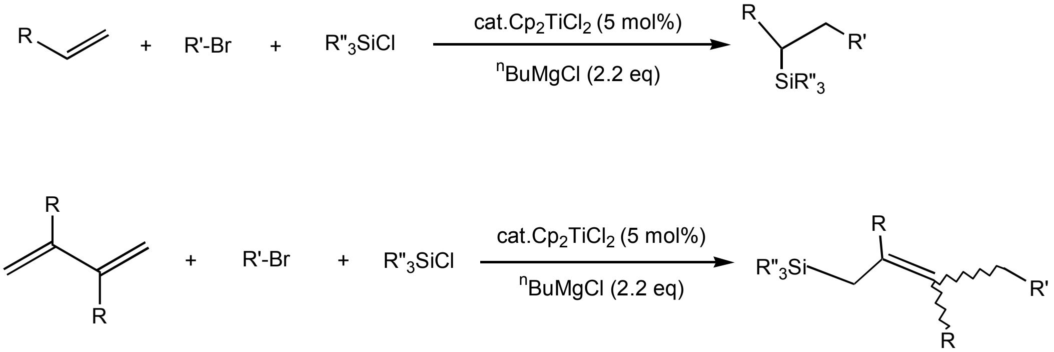
J. Am. Chem. Soc., 116, 8593 (1994)

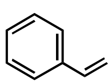
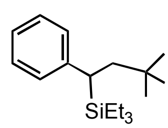
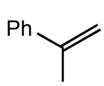
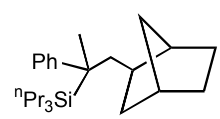
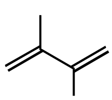
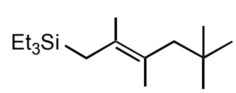
Reductive Opening of Epoxides



Angew. Chem. Int. Ed., 37, (1/2), 101 (1998)

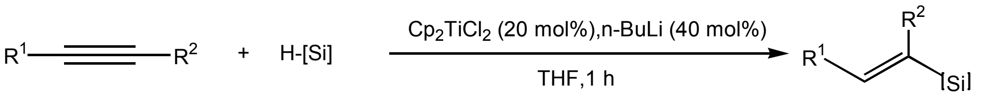
Carbosilylation of Alkenes and Dienes Using Alkyl Halides and Chlorosilanes



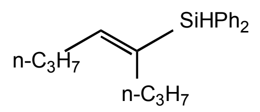
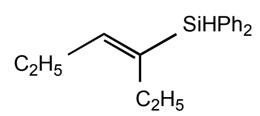
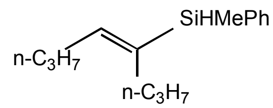
Starting Material	R-X	R'_3Si-Cl	Time(h)	Product	Yield(%)
	^{t}Bu-Br	Et_3Si-Cl	1		96
	2-Norbornyl-Br	$^nPr_3$Si-Cl	6		85
	^{t}Bu-Br	Et_3Si-Cl	2		83 E/Z=96/4

J. Org. Chem., 65, (17), 5291 (2000)

Regioselective syn-Hydrosilation of Alkynes



([Si] = $SiHPh_2$, $SiHMePh$, SiH_2Ph)

Alkyne	Hydrosilane	Alkenylsilane	Yield(%)
$n\text{-}C_3H_7C\equiv C\text{-}n\text{-}C_3H_7$	H-$SiHPh_2$		87
$Et\text{-}C\equiv C\text{-}Et$	H-$SiHPh_2$		96
$n\text{-}C_3H_7C\equiv C\text{-}n\text{-}C_3H_7$	H-SiHMePh		97

Org. Lett., 5, (19), 3479 (2003)

9. Storage and Safety Handling etc.

9-1. Storage

Store in a cool/dark place with reasonable ventilation.
Avoid direct radiation of sun beam to the container.

9-2. Handling

Unsealing (opening) of the container must be done under dry Nitrogen atmosphere. When resealing, the inner space of container must be filled with ample amount of dry Nitrogen gas. Titanocene Dichloride must be sealed very tightly and stored in a place mentioned above. Things (utensils, pipes, equipment, etc) which come in contact with this product must be well-dried before use. When solvent must be used, well-dehydrated micromoisture solvents is recommended.

9-3. First-aid Treatment

If Titanocene Dichloride adheres to a hand or face, it may cause allergic breakouts. It must be immediately washed off with ample amount of clean water.
For protection, please use the protective devices as follows:
Rubber gloves・Protective glasses・Dust-protection masks, etc

9-4. Fire Fighting Procedure

Titanocene Dichloride is a flammable chemical. If fire breaks out, move all the containers to a safe place where fire cannot reach. In case that this chemical catches a fire, use plenty of water or powder fire extinguisher to fight fire.

9-5. Waste Disposal

Waste disposal can be accomplished either by hydrolysis or by incineration. Hydrolyze in acid or alkaline aqueous solution to separate Titanium Hydroxide by neutralization. Burn with flammable solvent to give Titanium Oxide. Either waste must be disposed in accordance with industrial waste regulations.

■ The contents of this brochure are updated as of March, 2010.

■ Reference

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